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ENERGY-SAVING TECHNOLOGY FOR HOUSEHOLD PORCELAIN

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Paste compositions are worked out using quartz-feldspar raw material from Ukraine together with oxide mineralizers. The adoption of an energy-saving technology for household porcelain will make it possible to significantly lower the energy intensiveness of production and shorten the firing cycle.

Key words: low-temperature porcelain, mineralizer, phase formation, mullite, cordierite.

Firing costs are a significant fraction of the costs of manufacturing household porcelain articles. One of the main directions for decreasing energy consumption in the production of porcelain is the development and adoption of new pastes and glazes making it possible to lower the firing temperature, decrease the specific fuel consumption, increase the efficiency of the thermal equipment and reduce expenses associated with the wear of kiln furniture. It is known that the firing temperature can be lowered by introducing into paste small additions that intensify sintering and purposefully act on the porcelain phase-formation process [1].

The problem of the present work is to investigate the action of mineralizing additions on the formation of the phase composition of porcelain and the development of paste compositions for obtaining articles at firing temperatures to 1200°C using Ukrainian quartz-feldspar raw materials.

The radiative properties of pegmatites from the Lozovatskoe deposit (Kirovograd Oblast') and low-iron granites from the Anadol'skoe deposit (Donetsk Oblast') were determined in the course of the experimental work. It was shown that these materials are class-I radiation safe ($C_{eff} < 350$ Bq · kg^{-1}); this makes it possible to use them in the manufacture of household ceramics. The chemical composition of pegmatitic and granitic raw material as well as feldspar raw materials (FSM) from the enrichment of Lozovatskoe pegmatites were determined (Table 1).

The fluxing capacity of these materials was predicted using a previous method based on physical-chemical studies in systems of rock-forming oxides [2].

It was established that the most effective fluxes for low-temperature firing are Losovatskoe FSM and Anadol'skoe granite, which already at 1150°C form a significant amount of melt (> 95%) with relatively low viscosity 3.424 – 4.832 Pa · sec, surface tension in the range 0.275 – 0.286 N/m and elevated activity 0.103 – 0.155 arb. units, which attests to their promise as fluxing components in low-temperature porcelain pastes.

Porcelain pastes containing the following components were developed on the basis of the data obtained using simplex-lattice planning: clayey — VESKO-extra clay and Polozhskoe kaolin, fluxing — Lozovatskoe FSM and Anadol'skoe granite, inert — quartz sand from the Novoselovskoe deposit and technical alumina and modifiers – synthetic raw material (SRM) comprising a co-precipitated mixture of CaO and $Mg(OH)_2$.

The paste compositions making it possible to obtain low-temperature porcelain with the maximum sintering

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TABLE 1. Chemical Composition of the Experimental Raw Material

Components	Content, wt.%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	other
Anadol'skoe granite	72.22	15.89	0.87	–	0.81	0.12	4.51	3.70	1.88
Lozovatskoe pegmatite	75.92	13.25	1.11	0.04	0.65	0.19	4.73	3.61	0.38
Lozovatskoe FSM	67.99	18.13	0.10	0.04	0.64	0.21	8.26	3.95	0.52

TABLE 2. Effect of Mineralizers on the Phase Composition of Low-Temperature Porcelain

Mineralizer*	Quantitative phase composition of low-temperature porcelain, wt.%			Secondary phases
	α-SiO_2	α-Al_2O_3	$3Al_2O_3 \cdot 2SiO_2$	
CuO	18.60	3.38	16.88	Feldspars, magnesium spinel and cordierite
CîO	21.60	4.98	18.92	Feldspars
SnO_2	23.59	3.91	18.41	Feldspars, cordierite
Cr_2O_3	22.16	3.65	13.82	Feldspars

* The mineralizer content in the pastes was 0.3%.

(water absorption 0.12 – 0.15%), whiteness (70 – 72% according to the reflection coefficient) and transmittance (30 – 32%) contain the following raw materials (% by weight):

– granite-containing pastes: clayey — 37 – 40, fluxing — 53 – 56, modifying — 2 – 4, alumina — 5;

– pegmatite-containing pastes: clayey — 43 – 44, FSM — 28 – 30, modifiers — 6 – 8, alumina — 5 and sand — 15.

A drawback of the materials obtained is low bending strength (22 – 24 MPa), which is explained by the incomplete formation of the mullite phase during low-temperature heat-treatment. This led to a study of the possibility of intensifying mullite formation by introducing mineralizing additive.

In the technology of ceramic materials significant scientific and practical experience has been accumulated in using mineralizing additives, attesting to the efficacy of this technological solution [3]. In using such an approach in the technology of low-temperature porcelain the high brightness requirements for porcelain articles and the fact that in practice the conditions of low-temperature firing significantly limit the choice of mineralizer must be taken into account.

The effect of mineralizers on phase-formation processes for low-temperature porcelain was studied using the following oxides: CoO, CuO, SnO_2 and Cr_2O_3, whose amount by weight was varied in the range 0.1 – 0.3 %. A comparative analysis showed that these compounds differ significantly in regards to geometric and energy characteristics, which made it possible to determine the effect of the mineralizers chosen on the formation of the main crystalline phases of the products obtained by firing porcelain pastes.

The phase composition of the fired samples was studied by means of XPA. It was determined that mullite, corundum and a glass phase as well as residues of feldspars and quartz are present in the products of firing. When using copper and tin oxides as mineralizers cordierite and magnesium spinel were also identified in the phase composition of the products obtained by firing pastes. The quantitative determination of the content of the crystalline phases (mullite, corundum and quartz) was made using the internal standard method with calibration curves [4]. The results are presented in Table 2.

The studies showed that copper, tin and cobalt oxides are among the most effective mineralizing additives. However, the last one is not advised because at the concentration indicated the material is blue, which significantly lowers the whiteness of porcelain. The formation of a cordierite phase when using SnO_2 as well as cordierite and magnesium spinel with the introduction of CuO is a positive technological factor, since the indicated phases increase the thermal stability and strength of the materials obtained.

To determine the optimal amount of mineralizing additive for the present studies a first-order full factorial experiment (FFE) was implemented. The variable factors were the content (by weight) of the modifying phase X_1 (SRM) (2 – 6%) and one of the mineralizing additives (0.1 – 0.3%). The following characteristics were chosen as responses: water absorption W (%) and the content (by weight) of mullite and quartz in porcelain Q (%). A graphical interpretation of the dependences obtained for the samples containing mineralizing additives CuO and SnO_2 is presented in Fig. 1.

The morphology of the materials obtained was studied by IR spectroscopy (Fig. 2). The presence of mullite in the samples is confirmed by the presence of bands peaking at 878 – 915 cm^{-1} in the spectrum; these bands attest to the existence of aluminum ions in six-fold coordination. Bands belonging to aluminum-oxygen rings $[Si_5AlO_{18}]$ in the cor-

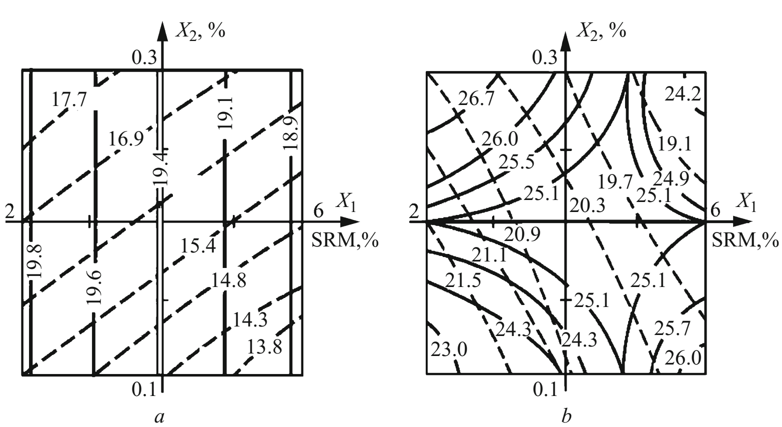

Fig. 1. Graphical interpretation of the FFE for samples of low-temperature porcelain (wt.%) with CuO (a) and SnO_2 (b) as mineralizers: – – – –) mullite, %; ——) quartz, %.

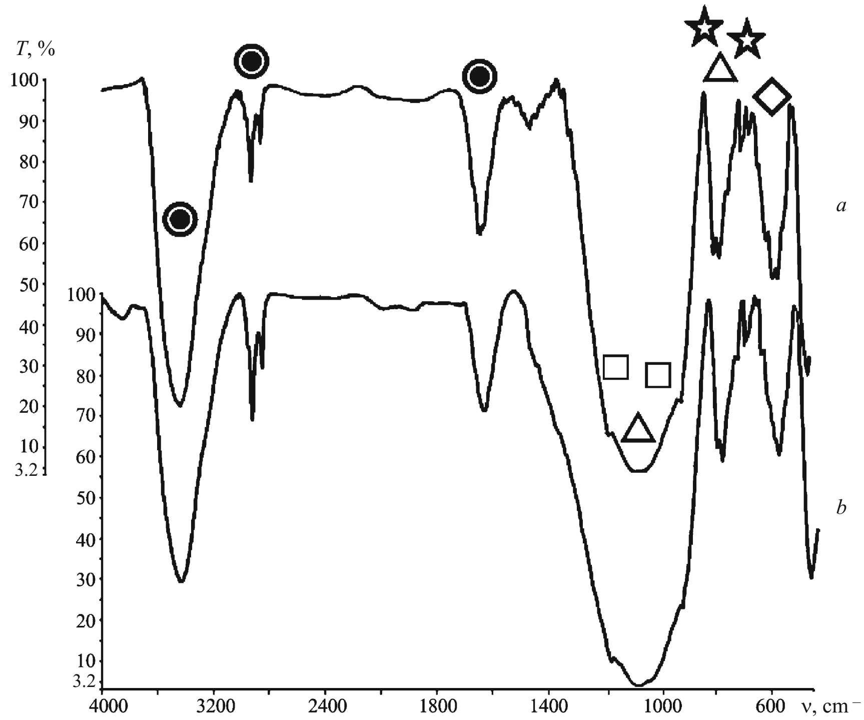

Fig. 2. IR spectra of porcelain samples containing SnO_2 (*a*) and CuO (*b*): ⦿) O–H; △) Si–O–Si; ◇) Si–O–Al; □) Al–O–Al; ✮) Si_5AlO_{18}; ○) Me–O.

dierite structure, peaking at 770 and 695 cm^{-1}, indicate the presence of a cordierite phase.

The formation of low-temperature porcelain during firing was studied by means of thermogravimetric, electron-microscopic, petrographic and quantitative x-ray phase analysis methods. Two exo effects characterizing the formation of crystalline phases (cordierite and primary mullite) were recorded in the thermogram (Fig. 3).

A characteristic of the phase composition and structure of the materials obtained by firing pastes at different temperatures (Fig. 4) makes it possible to record phase transformations as the porcelain cures.

A complex analysis of the results made it possible to determine the following mechanism of phase formation of low-temperature porcelain.

The presence of calcium-magnesium modifier (SRM) in the paste makes possible earlier formation of a high-activity melt (even at 950°C) with viscosity that is low because of depolymerization of the aluminum-silicon network. In turn, the mineralizing action of the additives SnO_2 and CuO is manifested in a change of the coordination state of the aluminum ($[Al]^{4+} \to [Al]^{6+}$). In the presence of melt and mineralizer short-prismatic crystals of primary mullite and cordierite are formed at temperatures 950 – 1000°C. Subsequent heating to 1050°C gives rise to active dissolution of the products of thermal destruction of clayey minerals in the liquid phase, as a result of which the melt is enriched with Al^{3+} and Si^{4+}. As temperature increases further (above 1100°C) the amount of melt increases and the Al^{3+} ions in it diffuse to-

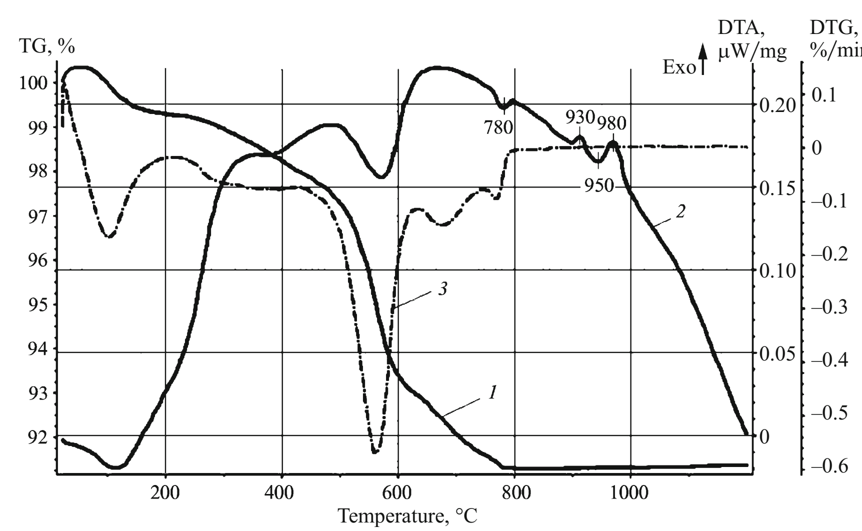

Fig. 3. Thermogram of a sample of low-temperature porcelain: *1*) TG, *2*) DTA, *3*) DTG.

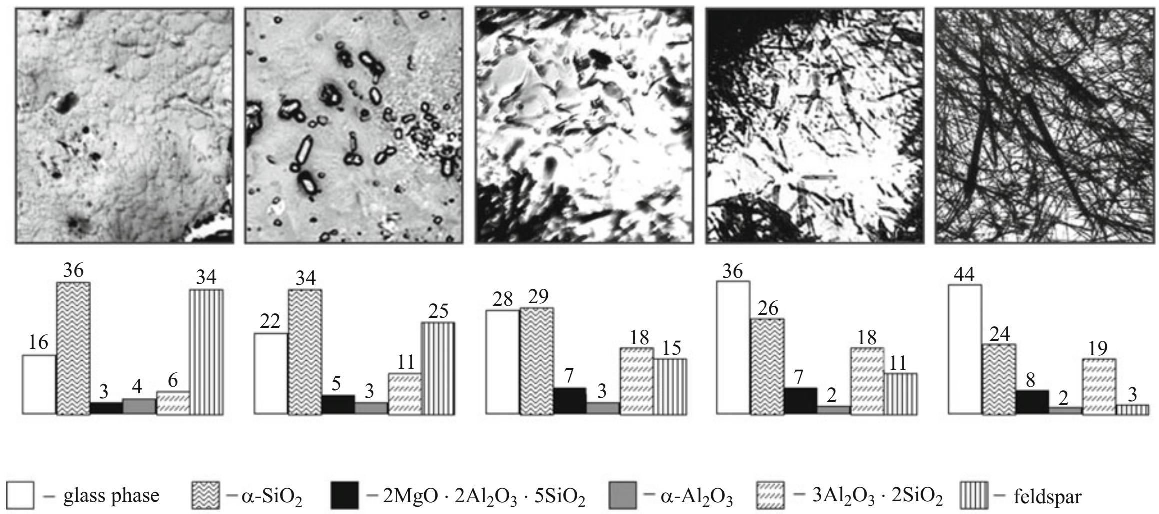

Fig. 4. Stages in the formation of the phase composition and structure of low-temperature porcelain. The numbers in the figure represent the content (wt.%) of the corresponding phases.

ward the centers of crystallization, which increases the sizes of the crystalline embryos. This is manifested in the formation of secondary (needle) mullite at 1150°C, whose crystals ranging in size from 0.02×4.0 to 0.3×5.0 μm are chaotically intertwined with one another and form a matted-fiber structure, making it possible to obtain dispersion-hardened material.

The data obtained served as a base for working out the composition of low-temperature porcelain using the product of enrichment of Lozovatskoe pegmatites as the fluxing component. The materials fired at 1150°C are characterized by a complex of high operating and aesthetic properties that determine the quality of porcelain articles: water absorption 0.1 – 0.3%, ultimate bending strength 50 – 55 MPa, whiteness (according to the reflection coefficient) 73 – 75% and translucency 31 – 34% with tile thickness 3 mm. The thermal stability of the articles glazed with non-fritted tin-containing glaze is 240°C. The observed increase of the strength and whiteness of the materials obtained is explained by the formation of a felt-like structure and hardening of the glass phase by disperse mullite formed in amounts to 18 – 20%. In turn, the presence of a cordierite phase increases the thermal stability of the manufactured articles.

CONCLUSIONS

In summary, pastes were developed using quartz – feldspar raw material from Ukraine and the technological parameters for obtaining low-temperature porcelain were determined. The particulars of its formation were determined — the material sinters with the participation of modified feldspar melt and intense formation of mullite and cordierite phases in the presence of oxide mineralizers, whose presence changes the coordination of the aluminum ions from the predominating tetrahedral to octahedral.

The adoption of the new energy-saving technology for household porcelain will lower substantially the energy-intensiveness of the products and shorten the firing cycle, which will give producers many advantages.

REFERENCES

1. G. N. Maslennikova, *Physical-Chemical Processes of Structure Formation in Porcelain* [in Russian], I. V. Grebenshchikov Institute of Silicate Chemistry, Nauka, Leningrad (1989) (Chemistry and Technology of Silicate and Refractory Nonmetallic Materials).
2. M. I. Ryshchenko, E. Yu. Fedorenko, M. A. Chirkina, et al., “Microstructure and properties of lower-temperature porcelain,” *Steklo Keram.,* No. 11, 26 – 29 (2009); M. I. Ryshchenko, E. Yu. Fedorenko, M. A. Chirkina, et al., “Microstructure and properties of lower-temperature porcelain,” *Glass Ceram.*, **66**(11 – 12), 393 – 396 (2009).
3. I. V. Emchenko, *Particulars of the Improvement of the Properties of Ceramic Articles by Intensification of Their Sintering* [in Russian], L’vov Commercial Academy, L’vov (2006).
4. L. S. Zevin and L. L. Zavyalova, *Quantitative X-Ray Phase Analysis* [in Russian], Nedra, Moscow (1974).